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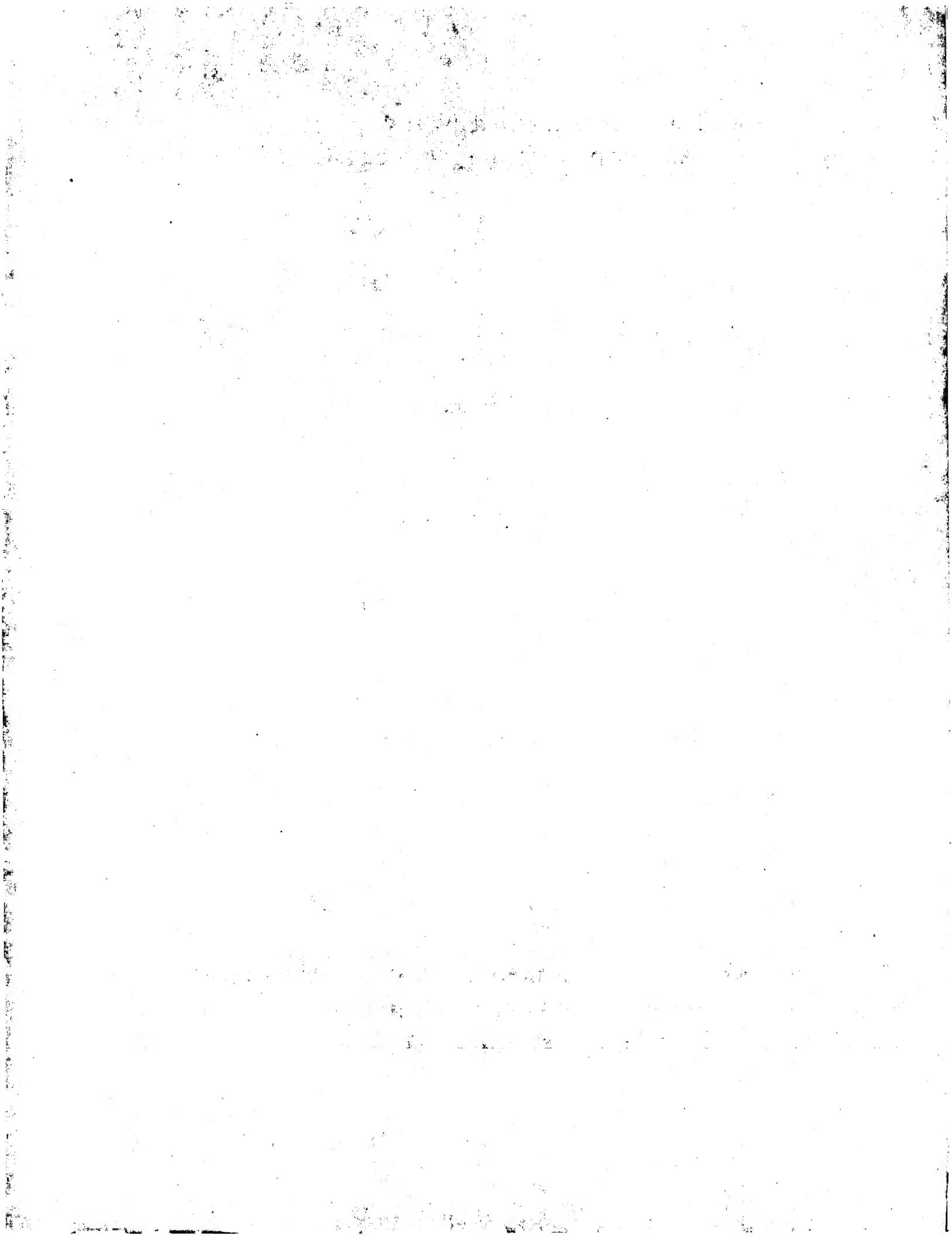
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(54) Laundry softening detergent  
(57) A heavy duty laundering and textile softening detergent composition, in particulate form, useful for automatic machine washing of laundry in water, especially hot water, and readily dispensable from a charging compartment of an automatic washing machine (by action of water being fed through such compartment) includes a synthetic organic detergent, a builder for such detergent and a laundry softening proportion of bentonite, with which there is present a dispensing assisting proportion of a silicate or similarly

functioning derivative of such silicate. In addition to tending to inhibit firm adherence to the charging compartment walls of the bentonite, which is advantageously in separately agglomerated bead form, and promoting release thereof from such walls, the silicate also aids in controlling the foaming activity of the built synthetic organic detergent and in strengthening the bentonite agglomerates. It also assists in stabilizing perfumes, dyes and bleaches, when such are present in the detergent compositions when it is employed in coatings for particles containing such components.

## SPECIFICATION

## Laundry softening detergent

The present invention relates to detergent compositions. More particularly, it relates to particular heavy duty laundering and textile softening detergent compositions intended for use in the machine washing of laundry. It also relates to methods for the manufacture of such compositions.

10      Betonite is advantageous as a softening agent in detergents. The softening properties of bentonite and its desirable adherence to substrates are important advantages but its "gelling" characteristics can cause an

15      objectionable gumminess in the detergent, which sometimes will tend to hold detergent beads and/or bentonite beads or agglomerates to surfaces, thereby tending to inhibit free flow. Thus, under conditions of high humidity or in the

20      presence of free moisture bentonite can "gel" and become sticky or of reduced flowability, even becoming held to passageway or chamber walls despite applications of forces to the particles to remove them (such as the force of flowing water

25      being charged to an automatic washing machine). Such adherence could be significantly disadvantageous for a desirably free flowing commercial particulate detergent product and could lead to a lesser degree of acceptance of the

30      product by the consumer. Even when flowability through production lines during the manufacturing and packaging processes, and flowability from the dispensing carton when the product is being employed by the ultimate

35      consumer are satisfactory, the presence of bentonite can cause the detergent composition particles to be held to appliance part walls, especially charging compartment walls, of washing machines equipped with means for

40      automatically charging detergent composition to the wash water in the machine tub or drum, when such particles and the bentonite present are moistened. In such circumstances the bentonite may tend to swell, with the production of moist

45      adherent surfaces, so that the particles may resist removal from surfaces against which they are resting. For example, in washing machines and other appliances equipped with automatic dispensers or charging compartments, the

50      detergent particles may not entirely fall from the dispenser or be washed out of the dispenser, especially if the dispenser walls had been wet before addition of the detergent. Failure to dispense part of the desired charge to the

55      washing machine diminishes the effective detergent and softener concentrations of the wash water and can lead to inaccurate detergent and softener concentrations being employed. Also, it may create an unsightly build-up which

60      may be objectionable to the consumer. In either situation the result is undesirable and should be avoided, if possible.

In accordance with the present invention a heavy duty laundering and textile softening

65      particulate detergent composition, useful for automatic machine washing of laundry in water and dispensable from a charging or dispensing compartment of such a machine by action of water being fed through such compartment,

70      comprises a built synthetic organic detergent which is an anionic or nonionic detergent or a mixture thereof, a building proportion of a builder for the synthetic organic detergent which is a water soluble or water insoluble builder or a mixture thereof, and a softening proportion of bentonite, with the bentonite being in particles with which there is included a dispensing assisting proportion, preferably at least 0.15%, of a silicate and/or dispensing assisting derivative

75      thereof. In preferred embodiments of the invention the synthetic organic detergent includes both an anionic detergent, which is preferably a sodium linear higher alkylbenzene sulphonate, and a nonionic detergent, which is preferably a

80      condensation product of a higher fatty alcohol and polyethylene oxide, a higher fatty acid soap is present, the builder salt is primarily pentasodium tripolyphosphate or NTA or a mixture thereof, with a small proportion of sodium silicate, the

85      bentonite is a swelling bentonite of a moisture content of at least 3%, the silicate is an alkali metal lower alkyl silicate, more preferably potassium methyl silicate, and 5 to 35% of a bleaching agent which releases oxygen in

90      aqueous solution at elevated temperature, such as sodium perborate, is present. Also within the invention are methods for making the improved products that have been described herein.

95      The synthetic organic detergent(s) employed

100      will normally be either nonionic or anionic and very preferably will be a combination of both, but suitable amphoteric or ampholytic detergents, such as those sold under the Miranol trademark may also be used in conjunction with nonionics

105      and anionics in the present compositions. Cationic detergents, such as the quaternary ammonium halides, e.g. those sold under the Arosurf trademark, can also serve as supplementary fabric softeners in these products

110      but normally will not be used.

115      Various synthetic anionic organic detergents, such as those characterised as sulphonates and sulphates, usually as alkali metal or sodium salts, may be employed, but those which are most preferred are the linear higher alkylbenzene sulphonates, higher alkyl or fatty alcohol sulphates and higher fatty alcohol polyethoxy or polyethoxylate sulphates. Preferably, in the higher alkyl benzene sulphonates the higher alkyl group

120      is linear and is preferably of 10 to 14 carbon atoms, more preferably 11 to 13, e.g. 12, and the sulphonate is a sodium salt. The alkyl sulphate is preferably a higher fatty alkyl or alcohol sulphate of 10 to 16 carbon atoms, more preferably 12 to

125      14 carbon atoms, e.g. 12, and is preferably also employed as the sodium salt. The higher fatty alcohol polyethoxy sulphates will preferably be of 10 to 18 carbon atoms, more preferably 12 to 16, e.g. 12, in the higher fatty alcohol, the ethoxy

content will preferably be from 3 to 30 ethoxy groups per mol, more preferably 3 or 5 to 20, and the detergent preferably will be a salt of sodium. Thus, it will be seen that the alkyl groups of the 5 sulphonates and sulphates are preferably linear or fatty higher alkyl groups of 10 to 18 carbon atoms, the cation is preferably sodium, and when a polyethoxy chain is present the sulphate is preferably at the end thereof. Other useful anionic 10 detergents include the higher olefin sulphonates and paraffin sulphonates, e.g. the sodium salts wherein the olefin or paraffin groups are of 10 to 18 carbon atoms. Specific examples of the preferred detergents are sodium dodecyl benzene 15 sulphonate, sodium tallow alcohol polyethoxy (3 EtO) sulphate, and sodium hydrogenated tallow alcohol sulphate. In addition to the preferred anionic detergents mentioned, others of this well known group may also be present, especially in 20 only minor proportions with respect to those previously described. Also, mixtures thereof may be employed and in some cases such mixtures can be superior to single detergents.

Although various nonionic detergents of 25 satisfactory physical characteristics may be utilized, including condensation products of ethylene oxide and propylene oxide with each other and with hydroxy-containing aromatic and aliphatic bases, such as nonyl phenol and Oxo- 30 type alcohols, it is highly preferred that the nonionic detergent be a higher fatty alkoxy poly-lower alkoxy lower alkanol, which may also be described as a condensation product of ethylene oxide (and/or propylene oxide) and a higher fatty 35 alcohol. In such products the higher fatty alkoxy or alcohol is of 10 to 16 carbon atoms, preferably 12 to 15 carbon atoms, and the nonionic detergent contains from about 3 to 20 lower alkoxy groups, preferably 5 to 15, and more 40 preferably 9 to 13 ethylene oxide groups per mol, e.g. 11.

The builder for the synthetic organic detergent, which helps to improve the washing action of the detergent, is either a water soluble or a water 45 insoluble builder or a mixture thereof. Of course, mixtures of water soluble builders may also be utilized, e.g. polyphosphate and NTA (nitrilotriacetic acid salt, normally the sodium salt), but of the water insoluble builders usually only the 50 zeolites will be present, although mixtures of such zeolites may also be found to be advantageous. While zeolites are useful components of the present compositions, generally it will preferably to employ water soluble builder(s), and often such 55 will be the only builder(s) present.

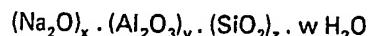
The water soluble builder or mixture thereof employed may be one or more of the conventional materials that have been used as builders or suggested for such purpose. These include 60 inorganic and organic builders, and mixtures thereof. Among the inorganic builders those of preference are the various phosphates, preferably polyphosphates, e.g. tripolyphosphates and pyrophosphates, such as pentasodium tripoly- 65 phosphate and tetrasodium pyrophosphate.

Trisodium nitrilotriacetate (NTA), preferably employed as the monohydrate and other nitrilotriacetates, such as disodium nitrilotriacetate, are preferred organic builders. The designation NTA, which normally stands for nitrilotriacetic acid, in this specification is employed to also refer to the various salts thereof, preferably the alkali metal salts and most preferably the trisodium salt. Sodium tripolyphosphate, sodium pyrophosphate 70 and NTA may be utilized in hydrated forms, which are often preferred, but anhydrous forms may also be used. Of course, carbonates, such as sodium carbonate, are useful builders and may desirably be employed, alone or in conjunction with bicarbonates, such as sodium bicarbonate. When the polyphosphates are employed it may be preferred to have sodium pyrophosphate present with sodium tripolyphosphate (STP) in proportion from 1:10 to 10:1, preferably 1:5 to 5:1 with 75 respect to STP, with the total proportion of both builders being about the same as that mentioned herein for the sodium tripolyphosphate. Other water soluble builders that are considered to be effective include the various other inorganic and 80 organic phosphates, borates, e.g. borax, citrates, gluconates, EDTA (ethylene diamine tetracetic acid e.g. as the sodium salt) and iminodiacetates. Preferably the various builders will be in the forms of their alkali metal salts, either the sodium or 85 potassium salts, or a mixture thereof, but sodium salts are normally more preferred. In some instances, as when neutral or slightly acidic detergent compositions are being produced, acid forms of the builders, especially of the organic 90 builders, may be preferably but normally the salts will either be neutral or basic in nature. The silicates, preferably sodium silicate of  $Na_2O:SiO_2$  ratio within the range of 1:1.6 to 1:3.0, preferably 1:2 to 1:2.8, e.g. 1:2.35 or 1:2.4, also serve as 95 builder salts but because of their strong binding properties and because they could promote objectionable adherence of detergent particles to dispenser walls they are considered to be special cases of builders, and relatively small proportions 100 builders, may be preferably but normally the salts will either be neutral or basic in nature. The silicates, preferably sodium silicate of  $Na_2O:SiO_2$  ratio within the range of 1:1.6 to 1:3.0, preferably 1:2 to 1:2.8, e.g. 1:2.35 or 1:2.4, also serve as 105 builder salts but because of their strong binding properties and because they could promote objectionable adherence of detergent particles to dispenser walls they are considered to be special cases of builders, and relatively small proportions 110 thereof will be present (such proportions will be described separately from the other builders). When it is desired for greater proportions of silicate to be in the detergent composition it may be preferable for hydrated sodium silicate 115 particles to be post-added to spray dried particles containing other builder(s).

The water insoluble builders, as that term is employed in the present specification, are those which help to improve the detergency of synthetic 120 organic detergents, especially that of synthetic anionic organic detergents, and in such cases the mechanism for increasing detergency appears to be related to water softening effects of the builder, such as calcium and/or magnesium ion 125 removal from the wash water, usually by an ion exchange mechanism. While it is within the invention to utilize water insoluble builders other than the zeolites, as a practical matter, at the present time, the zeolites are principal such 130 insoluble builders that are used.

The zeolites employed include crystalline, amorphous and mixed crystalline-amorphous zeolites, of both natural and synthetic origins. Preferably, such materials are capable of reacting sufficiently rapidly with calcium ions so that, alone or in conjunction with other water softening compounds in the detergent, they soften the wash water before adverse reactions of such ions with other components of the synthetic organic detergent composition occur. The zeolites employed may be characterised as having a high exchange capacity for calcium ion, which is normally from about 200 to 400 or more milligram equivalents of calcium carbonate hardness per gram of aluminosilicate, preferably 250 to 350 mg eq/g.

Although other ion exchanging zeolites may also be utilized, normally the finely divided synthetic zeolite builder particles employed in the practice of this invention will be of the formula



wherein x is 1, y is from 0.8 to 1.2, preferably about 1, z is from 1.5 to 3.5, preferably 2 to 3 or about 2, and w is from 0 to 9, preferably 2.5 to 6.

25 The zeolite should be a univalent cation-exchanging zeolite, i.e. it should be an aluminosilicate of a univalent cation such as sodium or potassium.

30 Crystalline types of zeolites utilizable as good ion exchangers in the invention, at least in part, include zeolites of the following crystal structure groups: A, X, Y, L, mordenite and erionite, of which types A, X and Y are preferred. Mixtures of such molecular sieve type zeolites can also be 35 useful, especially when type A zeolite is present. These crystalline types of zeolites are well known in the art and have been described in many patents in recent years for use as detergent composition builders.

40 Crystalline zeolites of ion exchanging and water softening properties that are preferred are those which are in hydrated or water loaded form, containing bound water in an amount from about 4% up to about 36% of the zeolite total weight,

45 depending on the type of zeolite used, and are preferably hydrated to about 15 to 70% of their capacities. Normally, water contents are in the range of about 5 to 30%, preferably about 10 or 15 to 25%, such as 17 to 22%, e.g. 20%.

50 Preferably the zeolite should be in a finely divided state, with the ultimate particle diameters being up to 20 microns, e.g. 0.005 to 0.01 to 20 microns, more preferably being from 0.01 to 15 microns, e.g. 3 to 12 microns, and especially 55 preferably being of 0.01 to 8 microns mean particle size; e.g. 3 to 7 microns, if crystalline, and 0.01 to 0.1 micron, e.g. 0.01 to 0.05 micron, if amorphous. Although ultimate particle sizes are much lower, usually the zeolite particles will be of 60 sizes within the range of No's. 100 to 400 sieve (U.S. sieve series, which have openings 149 microns across and 37 microns across respectively), preferably 140 to 325 (U.S. sieve

series, which have openings 105 microns across 65 and 44 microns across respectively). However, they may sometimes be agglomerated, separately or with spray dried detergent composition particles, to sizes like those of the particles, for example,  $\pm 10$  or 25%.

70 Although sodium sulphate and sodium chloride and other filler salts possess no building properties they are sometimes utilized in detergent compositions for their filling characteristics, and sodium sulphate is especially 75 useful as a processing aid. In addition to increasing the volume and weight of the product to facilitate measuring they also sometimes improve bead stabilities and physical properties of the detergent composition beads in which they 80 are incorporated. Nevertheless, because the present compositions are satisfactory without any fillers being present, such are often avoided entirely or any proportion thereof present may be minimized.

85 The softening clay that is an important component of the present detergent compositions is of the type characterised as "bentonite". Bentonites are colloidal clays (aluminium silicates) containing montmorillonite. They are of 90 varying composition and are obtainable from natural deposits in many countries, including Italy, Spain, U.S.S.R., Canada and the United States (principally Wyoming, Mississippi and Texas). The bentonites which are useful in accordance with 95 the present invention are those which have "lubricating" and dispersing properties, which appear to be associated with swelling capacity in water. Although some bentonites, principally those which may be characterised as calcium (or 100 magnesium) bentonites, have low or negligible swelling capacities, these may be converted or "activated" so as to increase such swelling capacity. Such conversion may be effected by appropriate treatment with alkaline material,

105 preferably aqueous sodium carbonate solution, in a manner known in the art, to insert a monovalent metal, such as an alkali metal, e.g. sodium (or potassium), into the clay structure in place of the divalent alkaline earth metal or magnesium. In 110 addition to improving the swelling capacity of the bentonite, which benefits fabric softening and dispensing capabilities thereof, the alkali or alkali metal carbonate solution treatment of the non-swelling clay or poorly flowing clay replaces, for 115 example, 5 to 100%, 10 to 90% or 15 to 50% of the exchangeable calcium and/or magnesium with sodium (or potassium), and thereby improves the exchange capacity of the clay for water hardness ions, such as those of calcium and 120 magnesium. The resulting byproducts, calcium carbonate and magnesium carbonate, are left with the bentonite, and appear to have desirable adjuvant properties in the final products.

125 Although ion exchange capacities of bentonites have been mentioned in the patent literature as being relevant to softening capacity, it is a feature of the present invention that good textile softening is obtainable with sodium bentonites of

comparatively low ion exchange capacities. Whether the swelling bentonite (also called sodium bentonite herein because in most cases the exchangeable metal will be sodium) is a naturally occurring clay or is obtained by alkali treatment of a non-swelling or poorly swelling bentonite, it may be used in the present textile softening detergent compositions. Treated Italian bentonites have been found to be especially useful and are considered most appropriate for products intended for European markets. For American markets Wyoming bentonite is often preferable and such does not have to be treated because it already contains sodium ion in the bentonite structure and has swelling properties. Analysis of a typical Italian bentonite (after alkali treatment) shows that it may contain 66.2% of  $\text{SiO}_2$ , 17.9% of  $\text{Al}_2\text{O}_3$ , 2.80% of  $\text{MgO}$ , 2.43% of  $\text{Na}_2\text{O}$ , 1.26% of  $\text{Fe}_2\text{O}_3$ , 1.15% of  $\text{CaO}$ , 0.14% of  $\text{TiO}_2$  and 0.13% of  $\text{K}_2\text{O}$ . A typical Wyoming or western bentonite (untreated) may contain from 64.8% to 73.0% of  $\text{SiO}_2$ , 14 to 18% of  $\text{Al}_2\text{O}_3$ , 1.6 to 2.7% of  $\text{MgO}$ , 0.8 to 2.8% of  $\text{Na}_2\text{O}$ , 2.3 to 3.4% of  $\text{Fe}_2\text{O}_3$ , 1.3 to 3.1% of  $\text{CaO}$  and 0.4 to 7.0% of  $\text{K}_2\text{O}$ . Thus, it is seen that the compositions of the bentonites are quite different although both types have swelling properties. It is considered that if the  $\text{Na}_2\text{O}$  content of the clay is at least about 0.5%, preferably at least 1% and more preferably at least 2% (the equivalent proportion of  $\text{K}_2\text{O}$  may also be taken into account), the clay will be satisfactorily swelling for the purposes of the present invention, with satisfactory softening and dispersing properties in aqueous suspension (the swelling of the bentonite facilitates breakup of the bentonite agglomerate). While it is expected that proportions of the various constituents of the swelling bentonites (which may herein be referred to as sodium bentonites, whether natural or "activated") within the ranges between the typical analyses given will result in useful components of the present compositions, it is also considered that the percentages of the components of the natural swelling bentonite may be raised or lowered about 10% and that the typical analysis of the treated bentonites may be expanded  $\pm 10\%$ , with the bentonites within those ranges still being useful. Additionally, other swelling bentonites may be substituted, at least in part. Generally, the useful bentonites will have swelling capacities of at least 1 or 2 millilitres per gram, more preferably at least 5 or 10 ml/g. Of course, higher swelling capacity bentonites will also be useful. Normally the range of swelling capacities will be from 5 to 30 ml/g and frequently will be in the 5 to 20 ml/g range.

The sodium bentonite or swelling bentonite preferably will be agglomerated before being blended with spray dried built detergent beads and any other adjuvants to be post-added. Such agglomeration will be carried out in known manner, as by utilizing a water or aqueous binder spray application to tumbling bentonite powder, extrusion, compaction, pan agglomeration or other technique. However, it is highly desirable

that the bentonite be in finely divided powder form before agglomeration so that, when the agglomerate breaks up in the wash water, the particles of bentonite will be small enough to be effective lubricants, as deposited on the laundry. Thus, it will normally be desirable for essentially all of the bentonite powder, before agglomeration, to pass through a No. 100 sieve (U.S. Sieve Series which has openings 149 microns across), with at least 99% passing such a sieve and with over a major proportion thereof passing through a No. 200 sieve (U.S. Sieve Series, which has openings 74 microns across), preferably with less than about 30% by weight of the particles failing to pass through such a sieve and more preferably with no more than 20% resting on such sieve. Of course, the ultimate particle sizes are lower. Also important to promote ready break-up of bentonite agglomerates and dispersion in the wash water, so that the minute particles thereof may be adhered to textile fibres to soften them, is the moisture content of the bentonite. Although it is desirable to limit the free moisture content of the bentonite utilized to about 10% or so, with moisture contents above 15% not normally being employed, it is even more important to make certain that the bentonite includes enough free moisture, most of which is considered to be present between adjacent plates of bentonite, to facilitate quick disintegration of the bentonite and any adjacent materials in the particles when such particles or detergent compositions containing them are brought into contact with water, such as wash water. It has been found that at least about 2%, preferably at least 3% and more preferably, about 4% or more of water should be present in the bentonite (so-called "internal" moisture), and that the bentonite should not be dried so that less than such percentages of water are even temporarily present in it. In other words, over-drying to the point where the bentonite loses its internal moisture can significantly diminish the utility of the present compositions. When the bentonite moisture content is too low the bentonite does not aid in satisfactorily swelling and disintegrating the agglomerated beads in the wash water.

Preferred swelling bentonites of the types described above are sold under the trade names Laviossa and Winkelmann, e.g. Laviosa AGB and Winkelmann G 13, both of which are treated Italian bentonites, and Mineral Colloid No. 101 (and other similar designations) corresponding to Thixo-Gels No's. 1, 2, 3 and 4 (marketed by Benton Clay Company, and affiliate of Georgia Kaolin Co.). As will be described later, the treated bentonites will also preferably be essentially free of grit, preferably having been further processed by grinding to a fine powder before agglomeration. Usually the commercial bentonite used will have a pH in water (at 6% concentration) in the range of 8 to 9.4, a maximum free moisture content of about 8%, a specific gravity of about 2.6 and a viscosity, at

10% concentration in water, within the range of 5 to 30 centipoises, preferably 10 to 30 cp.

The silicate, which is employed in conjunction with the bentonite, preferably to coat

5 it, and which also can be used to coat the detergent composition particles, and which acts to inhibit sticking of the bentonite and the detergent to charging compartment walls of an automatic washing machine (and to walls of other 10 "containers" for the product), is one which may be easily applied to the bentonite and which can at least partially coat the particles thereof and inhibit their adhesion to walls of a compartment in which they may be stored temporarily, even

15 when such walls are damp or wet. The silicate is a salt of silicic acid, preferably an alkali metal salt thereof, and the silicic acid is preferably a lower alkyl silicic acid. While it is desirable that the salt-forming metal or other

20 cation be one which will produce a water soluble silicate, so that it may be applied to the bentonite in aqueous solution, such may not be necessary and it is contemplated that water dispersible siliconates will also be utilized.

25 Furthermore, it is within the invention to employ lipophilic siliconates, which may be applied in organic solvent solution or in aqueous organic solvent solution, or in corresponding emulsions or dispersions. The alkali metal of the silicate is 30 preferably either sodium or potassium, but other salt-forming cations may also be utilized providing that the silicate is suitable for the present purposes. It is contemplated that other alkali metal salts of silicic acids than the lower

35 alkyl siliconates may be utilized, including both aliphatic and aromatic siliconates, but the lower alkyl siliconates, wherein the lower alkyl is of 1 to 3 or 4 carbon atoms, e.g. potassium methyl silicate and sodium propyl silicate, are

40 considered to be preferred. Instead of employing the silicate an equivalent charge of the corresponding silicic acid and a corresponding base may be utilized.

For most effective results it is much preferred 45 to employ the lower alkyl siliconates previously described but it is recognized that such compounds may polymerize, at least partially, to silicic or other film-forming and foam-inhibiting compounds or polymers and accordingly it is 50 within the broader bounds of this invention to utilize such "derivative" materials directly, at least in part, as a component of the present detergent compositions. When such a derivative of the silicate is employed it will be one which aids in 55 improving the dispensing of the bentonite beads or detergent composition particles from a charging compartment of an automatic washing machine, such as a compartment wherein the particulate contents are washed out by the flow of 60 water into the washing tub of the machine.

Although the operation of the present invention should not be considered to be limited by the mechanism to be described, it may well be that the water soluble alkali metal lower alkyl 65 siliconates (which may also be described as alkali

metal lower alkyl silanates), may be converted to polymethyl siloxanes, as by the action of atmospheric carbon dioxide or other acidic acting material, which could also result in the production

70 of alkali metal carbonate, such as sodium carbonate, a useful builder salt. The polymethyl siloxanes are known to be hydrophobic and it is possible that their presence is the cause of the improved properties of the coated bentonite (or

75 other detergent particles) with respect to being of improved dispensing properties from the charging compartment of an automatic washing machine. The production of siloxanes by the described reaction has been mentioned in the text

80 *Chemistry and Technology of Silicones*, by Walter Noll, published by Academic Press in 1968. However, although silicones have been included in detergent compositions in the past, often for their anti-foaming properties, no disclosure of the

85 use of water soluble siliconates to coat bentonite and detergent particles to promote free release from damp surfaces of charging compartments, as in the present invention, is known and such process and the resulting compositions are

90 considered to be unobvious from the prior art.

The water soluble soap, which is a desirable component of the present detergent compositions and which has a useful foam limiting action in the wash water, which is especially advantageous for 95 side loading or horizontal tub washing machines, is normally a higher fatty acid soap of an alkali metal, such as sodium or potassium, with sodium soaps being highly preferred. Such soaps are well known and need not be described at length.

100 Suffice it to say that they may be made from natural fats and oils, such as those from animal fats and greases and from vegetable and seed oils, for example, tallow, hydrogenated tallow, coconut oil, palm kernel oil, and correspondent

105 "natural" and synthetic fatty acids, and that they are normally of 10 to 24 carbon atoms, preferably 14 to 18 carbon atoms. Preferably such soaps are of hydrogenated tallow or hydrogenated tallow fatty acids, e.g. stearic acid. The water soluble

110 soap which may be included in the present compositions will preferably be chosen so as to have a desirable balance of good detergent properties, effective foam reducing effect and other good physical properties. Specifically,

115 among those other physical properties will be desirable hardness, good binding effect and little or no tendency to produce adhesive gels under use conditions (as in the washing machine charging compartment). It has been found that

120 the sodium hydrogenated tallow soaps satisfy these conditions best but even compositions containing them are desirably also treated with silicate to further inhibit adhesion to damp compartment walls. Of course, for compositions

125 wherein foaming is desirable the soap content is lowered, the soap is omitted or a lower fatty acid soap, e.g. sodium laurate, may be used instead.

Bleaching agents do not have to be incorporated in all of the detergent compositions 130 of this invention but for best cleaning and

whitening of laundry it is often preferable that a bleach be employed. When the wash water temperature in the automatic washing machine is high enough sodium perborate is the bleaching agent of choice because the elevated temperature, especially when it is above 80°C, e.g. 90°C or 95°C, can cause decomposition of the perborate and release of bleaching oxygen from it. Thus, under such conditions the sodium perborate, which is often referred to as sodium perborate tetrahydrate or sodium borate perhydrate, and which will usually have an active oxygen content of at least about 10%, releases such oxygen without the need for employment of an activating agent or decomposition catalyst. When lower temperature laundering is undertaken, either in cold water or hot water, for example, at temperatures from 20°C to 60°C, the sodium perborate will not usually sufficiently decompose to satisfactorily bleach textiles being washed and in such circumstances an activator will be employed or another suitable bleaching agent will be used, also usually with an activator. Many such systems have been described in the literature, most of which belong to the class of peroxygen compounds, such as persulphuric acid, peracetic acid, performic acid, perphthalic and perbenzoic acid, and salts thereof, such as the alkali metal and alkaline earth metal salts, e.g. sodium or magnesium salts. Various activators for such compositions are known which promote the controlled release of oxygen from them in hot and cold water systems. Included among such activators are heavy metal salts, such as copper salts, and various inorganic and organic compounds, which have been described in the art. Among the lower temperature bleaches that which is preferred is magnesium dimonoperoxyphthalate. Of course, various other oxygen releasing bleaching materials, such as the hydroperoxides, may be employed and in the proper circumstances chlorine releasing bleaching materials can be incorporated in the present detergent compositions.

Various adjuvants may be present in the crutcher mix from which base beads or detergent compositions may be spray dried, or such adjuvants may be post-added, with the decision as to the mode of addition often being determined by the physical properties of the adjuvant, its resistance to heat, its resistance to degradation in the aqueous crutcher medium, and its volatility. Among the adjuvants often employed are enzyme powders or prills, which normally are post-added to the base heads because they are heat sensitive. These may be any of a variety of commercially available products, included among which are Alcalase (Registered Trade Mark), manufactured by Novo Industri, A/S, and Maxatase (Registered Trade Mark), both of which are alkaline proteases (subtilisin). Among specific enzyme preparations that may be employed are Novo Alcalase 2M (2 Anson units per gram) and Maxatase P 440,000. Although the alkaline proteases are most frequently employed, amylolytic enzymes, such as

alpha-amylase, may also be utilized. These enzyme compositions usually contain active enzymes in combination with an inert powdered vehicle, such as sodium or calcium sulphate, and the proportion of active enzyme may vary widely, usually being from 2 to 80% of the commercial preparation. In this specification proportions referred to are of the enzyme preparations, not the active part thereof.

Among the fluorescent brighteners those most commonly employed are the stilbene brighteners, e.g. Tinopal 5 BM, especially in extra concentrated form. Among the stilbene compounds are cotton brighteners, such as those sometimes referred to as CC/DAS brighteners, derived from the reaction product of cyanuric chloride and the disodium salt of diaminostilbene disulphonic acid, including variations thereof with respect to substituents on the triazine and aromatic rings. This class of brighteners is known in the detergent art and will most often be used when bleaching components are not present in the final product. When it is desired for the detergent composition to include a bleach, such as sodium perborate or other oxidizing bleach, bleach stable brighteners may be incorporated in the crutcher mix. Among these there may be mentioned the benzidine sulphone disulphonic acids, naphthotriazolyl stilbene sulphonic acids and benzimidazolyl derivatives. Polyamide brighteners, which also may be present, include aminocoumarin on diphenyl pyrazoline derivatives, and polyester brighteners, which can also be used, include naphthotriazolyl stilbenes.

Such brighteners are normally used as their soluble salts, e.g. sodium salts, but they may be charged as the corresponding acids. The cotton brighteners will usually comprise major proportions of the brightener systems employed.

When it is desired that the product made be entirely or partially coloured, various suitable dyes and dispersible pigments may be employed. When blue dyes, such as Acilan blue, or pigments, such as ultramarine blue, are utilized they have their dual effects of serving to colour some or all of the detergent composition particles, or particles of components of the detergent composition, and helping to give the washed laundry a desirable bluish tint. Colouring of agglomerated bentonite particles by suitable dyes or pigments may be especially desirable because natural bentonite sometimes may be off-colour, so that the agglomerates may be converted from particles that look dirty to those which are of attractive colour and appearance.

Perfumes employed, which are usually heat sensitive and may contain volatile constituents, including a solvent, such as alcohol or a suitable glycol or polyol or hydrocarbon, are normally of synthetic perfumery materials, sometimes mixed with natural components, and generally will include alcohols, aldehydes, terpenes, fixatives and/or other normal perfume components, known in the art.

In addition to the adjuvants mentioned there

may also be present flow promoting agents, anti-setting materials employed to prevent premature gelation of the crutcher mix, dispersion aids, anti-redeposition agents and, in some cases,

5 additional softening agents, e.g. cationic softeners such as the quaternary ammonium halides, e.g. dimethyldioctadecyl ammonium chloride. However, as was indicated previously, normally the cationic softening agents will not be

10 employed and if used, they will be post-added. Of course, water is present in the crutcher from which the spray dried component of the present composition is made, wherein it serves as a medium for dissolving or dispersing the various

15 components of the spray dried beads. Therefore, some water, in both free and hydrate forms, is in the product. Similarly, water may be employed to agglomerate the bentonite and perborate powders and dissolve the siliconate. While it may

20 be preferred to employ deionized water, so that the hardness ion contents thereof may be very low and so that metallic ions that can promote decomposition of any organic materials which may be present will be minimized, city or tap

25 water may be utilized instead and sometimes, for economic or supply reasons, will be used exclusively. Normally the hardness content of such water will be not greater than about 300 parts per million, as calcium carbonate.

30 The proportions of the various components in the final product of this invention will be such as to result in it being effective as a fabric softening detergent, free flowing and of improved dispensability from a charging compartment of an

35 automatic washing machine by action of wash water passing through such compartment. The proportion of anionic detergent will normally be from 3 to 10% of the final product, preferably 3 to 7% and more preferably 4 to 6%, e.g. 5%. Usually

40 the nonionic detergent content will be from 1 to 5%, preferably 2 to 4%, e.g. 3 or 4%. In those instances when nonionic detergent is not being employed the proportion of anionic detergent may be increased by as much as 5% and in cases in

45 which the anionic detergent is omitted the nonionic detergent content may be increased by up to 10%, providing that the detergent composition remains satisfactorily dispensable. While it is possible for effective detergent

50 compositions to be made without either the anionic or nonionic detergent, such products will not be as useful as preferred compositions of this invention. The builder content will generally be in the range of 20 to 75%, preferably 30 to 50%

55 (and such is often preferably entirely water soluble builder salt) and more preferably 30 to 40%, e.g. about 35%. As was previously indicated sodium tripolyphosphate and NTA are preferred water soluble builders, which may be the sole

60 builders employed. When they are utilized in admixture the mixture will preferably contain from 10 to 90% of one of them, with the balance being the other such builder, and within such ranges preferred proportions may be 20 to 80% and 40 to

65 60%, and complementing percentages. Similar

ranges of percentages are applicable when the builder is a mixture of water soluble builder salt and water insoluble builder, such as a zeolite.

The bentonite content of the textile softening

70 detergent, preferably in the form of a siliconate coated agglomerate of more finely divided bentonite powder particles, will be a satisfactorily softening proportion thereof, which usually will be within the range of 5 to 25%, preferably 10 to 20%, more preferably 14 to 18%, e.g. about 16%. The siliconate used will be employed in a proportion sufficient to have the desired dispensing assisting effect and such proportion will normally be from 0.05 to 1%, preferably 0.15

80 to 1%, although up to 3% can be employed. A preferred range of proportions of the silicatone is from 0.1 or 0.15 to 0.3 or 0.4%, for examples; 0.15% or 0.3%. When the siliconate is used to cover agglomerated bentonite only, on a coated

85 bentonite agglomerate basis the siliconate content will usually be at least 0.15%, often 0.15 to 5%, preferably 0.15 to 1% and more preferably 0.15 to 0.5%, e.g. 0.4%. When a fatty acid soap is present the

90 proportion thereof will usually be no greater than 10%. A preferred range of soap contents is from 2 to 6%, more preferably from 2 to 4%, e.g. 3%. When a bleaching agent is present the proportion thereof will usually be within the range of 5 to

95 35%, preferably 15 to 25%, e.g. 20%. However, it will be kept in mind that such proportions are based on employment of sodium perborate and will be modified when other oxidizing agents are utilized, so as to have approximately the same

100 bleaching effect (or active oxygen content). The moisture content of the product, which does not include hydrate moisture which is not removable during the standard heating at 105°C for two hours, will usually be within the range of 3 to

105 20%, with the higher percentages thereof being permissible when a substantial proportion, at least 1/4 and preferably at least 1/2 of the moisture is in hydrate form. A preferred such content is from 10 to 15%, e.g. 10%. Any

110 moisture not removable by the standard test mentioned above is considered to be a part of the compound in which it is present as a hydrate, e.g. a zeolite. The total proportion of various adjuvants which

115 may also be present in the detergent composition will usually be no more than 20%, preferably being limited to 15% and more preferably to 10%. Although water soluble sodium silicate has building properties, especially with respect to its

120 action against magnesium ions in hard water, because it also acts as a binder the proportion thereof present will not be limited by the builder content proportions previously given and will be considered herein with other adjuvants for the

125 present compositions. Usually it will constitute no more than 8% of the product, with a normal range of 1 to 5%, preferably 2 to 4%, e.g. 3%. The content of filler salt, such as sodium sulphate, when it is present, will also normally be limited, to

130 no more than 10%, and will normally constitute

from 0.5 to 5%, preferably 0.5 to 2%, e.g. 1 or 1.5% of the product. The percentage of proteolytic enzyme used will normally be from 0.1 to 2%, preferably 0.2 to 1%, e.g. 0.3%, and the percentage of optical brightener dye will be from 0.1 to 2%, preferably 0.1 to 0.5%, e.g. about 0.2%. Perfume content will normally be from 0.05 to 2%, preferably 0.1 to 1, and more preferably 0.2 to 0.5%, e.g. about 0.3%. Among other 10 adjuvants it may sometimes be desirable to have present small proportions of particulate sequestering agents and flow promoters. Among such materials a preferred sequestrant is diethylenetriamine pentaacetic acid, magnesium 15 salt (magnesium DTPA) but other diethylenetriamine acetates may be substituted for it. Magnesium silicate is a preferred flow promoter, which also may serve as a carrier for the sequestrant. Commercially, a mixture of such 20 products is available comprising 15% of the magnesium DTPA and 85% of  $MgSiO_3$  and when such is employed the proportion thereof is preferably from 0.1 to 1%, more preferably 0.1 to 0.5%, e.g. 0.2%. Proportions of the sequestrant 25 (or stabilizer) may be from 0.01 to 0.2%, preferably 0.02 to 0.1%, and for the  $MgSiO_3$ , concentrations are in the range of 0.1 to 0.9%, preferably 0.2 to 0.5%. Amounts of other adjuvants employed will be such as to accomplish 30 the purpose for which the adjuvant is included in the detergent composition but normally such proportions will not be in excess of 1 to 2% and frequently will be within the range of 0.05 to 1%.

In addition to the detergent composition 35 containing synthetic organic detergent, builder, bentonite and silicate, with soap, bleach and adjuvants often also being present, also within the present invention are silicate-treated bentonite, silicate-treated perborate and silicate-treated 40 enzyme. For the silicate-treated bentonite the silicate content will be from 0.2 to 10%, preferably 0.5 to 5% and more preferably 1 to 3%. For the corresponding detergent composition without bentonite and for the 45 enzyme and perborate the proportions of silicate will be the same as those for the final detergent composition but such proportions may be increased from 10 to 100%, depending on conditions and the proportions of the various 50 adjuvants in the detergent composition.

To make the products of this invention, known spray drying, agglomerating and mixing techniques (preferably all three) may be employed. Because such are not considered to be 55 significant features of the invention they will be referred to only briefly herein. In the spray drying operation a crutcher mix containing various components desired to be present in the spray dried bead and sufficiently stable to withstand the 60 crutching and spray drying operations, such as detergent, builder and suitable adjuvants, is spray dried from an aqueous crutcher mix, which normally will contain from about 40 to about 70 to 75% of solids, preferably 50 to 65% thereof, 65 with the balance being water. The crutcher mix

may contain the anionic detergent and a portion or all of the nonionic detergent, although usually no more than 5% of nonionic detergent (on the basis of the final product) will be in the crutcher 70 (the rest, if any, being post-added). All of the builder or mixture of builders will normally be added in the crutcher, although this is not necessary. The bentonite powder is separately agglomerated and is post-added to the spray 75 dried product but sometimes it may be incorporated in the crutcher mix. Aqueous silicate solution, stable fluorescent brightening dye, soap and filler salt are usually added in the crutcher, together with any stable pigment and other 80 colourants that may be employed. Instead of charging a neutralized detergent, the crutcher may be utilized as a neutralizing vessel, in which anionic organic detergent acid is neutralized with aqueous caustic. Such acid, for example, may be 85 dodecylbenzene sulphonic acid containing about 45 to 50% of active ingredient, which may be neutralized with an aqueous sodium hydroxide solution, such as one containing 38% of  $Na_2O$ . If the detergent acid is made by sulphonating the 90 alkylbenzene with sulphur trioxide the active ingredient content of the acid may be as high as 99%. A higher fatty acid mixture may also be neutralized in the crutcher with the detergent acid to produce a desired higher fatty acid soap- 95 detergent mixture.

The crutcher mix may be spray dried in a conventional spray tower, utilizing either concurrent or countercurrent flow. Normally the mix will be at a temperature in the 20 to 80°C 100 range, preferably 40 to 70°C and will be spray dried in a tower in which the drying air is at a temperature of 200 to 400°C, to produce spray dried beads of particle sizes in the range of No's 10 to 100 (U.S Sieve Series) sieves. Any particles 105 that are outside the desired range may be removed by screening and may be reprocessed. The beads thus made have a bulk density in the range of 0.3 to 0.6 g/ml, e.g. 0.5 g/ml. They are of a moisture content in a range which may be as 110 broad as about 3 to 20% but normally will be about 10 to 15%.

After production of the spray dried portion of the compositions other components thereof may be mixed with the beads or sprayed onto them 115 (and onto other components of the product, when desired). Generally it will be preferred for the bentonite, enzyme, bleach, and any other particulate products, such as those in powder, agglomerate or prill form (except the silicate), which are 120 intended to be post-added to the spray dried beads, to be mixed with them, after which any liquids (including silicate in solution) to be post-added may be sprayed onto the mixture. However, orders of post-addition of components 125 may be varied and sometimes part of the particulate material may be post-added after one or more of the liquids. Two or more of the particulate materials may be pre-mixed before post-addition and similarly, mixtures of liquids 130 may also be made.

Solvents may be employed for various components to be applied as liquids and in some cases emulsions may be employed. Thus, while the siliconate is preferably applied in the solution form, in water, if a less soluble siliconate is employed it may be applied as an aqueous emulsion. In some instances it may be desirable to utilize the siliconate in an aqueous emulsion with perfume and/or nonionic detergent.

10 However, it is much preferred first to coat the unperfumed detergent composition with an aqueous siliconate solution spray and subsequently to spray perfume onto the "siliconated" product. In some instances it may be desirable to extend the perfume with a suitable solvent, such as a comparatively odourless alkylate (hydrocarbon). Instead of spraying the siliconate onto the mixture of spray dried (or otherwise manufactured to similar product characteristics) detergent beads, bentonite agglomerate, enzyme prills or agglomerates, and perborate particles in mixture, the siliconate may be applied to such individual components separately or in various combinations. Such can be accomplished with separate sprays of siliconate, in which case the proportion thereof deposited on the different components may be readily controllable, or a single siliconate spray may be directed onto different feed streams of such components as they enter a suitable mixer. When nonionic detergent is post-added (and it will sometimes be preferred that all of the nonionic detergent be added in the crutcher so that the siliconate will be of greatest dispensing assisting effect) it may be sprayed onto or otherwise satisfactorily applied to the surfaces of the spray dried beads before admixing with the other particulate components of the final product and before application of siliconate spray thereto.

40 Also, as previously indicated, the nonionic detergent, in liquid form, may be mixed with the siliconate and/or perfume to be sprayed onto the product, in which case it may act like an emulsifier.

45 The apparatus for effecting the various mixings and sprayings is known in the art and accordingly will not be described in detail herein. Spraying may be through conventional nozzles, usually of wide spray pattern design, but other types of spraying equipment may also be employed. The mixers may be of various designs but preferably include revolving inclined tubes or drums, inside which spraying may be effected. However, the V-shaped blenders, especially those of continuous feed design, and other commercial powder blenders can also be satisfactory.

50 The amount of siliconate that will be sprayed onto the surfaces of the various particulate components of the detergent composition will be such that the final product includes a dispensing assisting proportion of the siliconate (or a derivative thereof). Because it is thought that the bentonite agglomerates can to some extent interfere with satisfactory dispensing of the particulate detergent composition from the feed

chamber of an automatic washing machine (of the "European type"), it may be preferable for a greater proportion of siliconate to be applied to such bentonite agglomerate particles, e.g. up to 70 5%, when such is feasible. In some cases only the bentonite particles will be treated with the siliconate, in which instances the proportion of siliconate in the final detergent composition may often be decreased, e.g. by as much as 50%.

75 Applications of the siliconate involve addition of moisture to the composition being treated, when the siliconate is in aqueous solution or emulsion (but not if in non-aqueous solution). Such can either be desirable or not, depending on the 80 moisture content and the properties of the detergent composition and processing apparatus. Accordingly, the concentration of siliconate in the spray liquid may be adjusted. Of course, the greater the volume of the spray and the greater 85 the dilution of the siliconate the more uniformly a spray may be distributed on the particulate material. On the other hand, if the product is borderline or too high in moisture concentration a dilute siliconate spray may exacerbate this 90 condition. Generally the concentration of siliconate in the liquid will be at least 5%, and preferably will be at least 10%. Because the siliconate is completely miscible with water higher concentrations may be employed, which 95 are usually within the ranges of 5 or 10 to 25 or 50%.

The various mixing and spraying operations will normally take place at about room temperature but operations in the range of 10 to 100 40°C, preferably 20 to 30°C are preferred. The particle sizes of the materials being coated with siliconate will usually be like those of the final product, within the No's. 10 to 100 or 200 sieve (U.S. Sieve series) range (the perborate and 105 enzyme ranges may extend to No. 200). The agglomerated bentonite particles will be those resulting from agglomeration or compaction of more finely divided particles, such as those of which over 50% pass through a No. 200 sieve 110 (U.S. Sieve Series, which has openings 74 microns across). Such particles will be essentially grit-free and will normally have from 0.05 to 0.15 to 3 or 5%, preferably 0.1 or 0.15 to 0.5 or 1% of siliconate, such as potassium methyl siliconate or 115 sodium propyl siliconate, sprayed onto the surfaces thereof to at least partially coat such surfaces. They may be coloured with a suitable dye or pigment, such as Acilan Brilliant Blue FFR, or such or other suitable colourant may be applied 120 with the siliconate. The siliconate does not obscure the colour. Sometimes the bentonite agglomerates may be larger than the other particles in the product, e.g. 10 to 50% greater in diameter, to accentuate their difference. In many 125 instances the bentonite agglomerates will preferably be of sodium carbonate treated bentonite (such treatment improves the colour of off-colour clay) and will contain magnesium carbonate and/or calcium carbonate therein, 130 resulting from such treatment. When the particles

are only partially coated with silicate it is desirable for at least 10% of the surface area (of the equivalent spheres) to be covered by the silicate, and more preferably a greater percentage will be covered, e.g. 50%, to facilitate dispensing. Similar considerations and conditions apply when the enzyme, bleach and detergent particles are being treated, with the exception that in such cases a lesser proportion of silicate may be employed than that used for coating bentonite agglomerates.

In the various cases mentioned above the coating of the solid silicate will normally be on the outer 1% of the thicknesses of the particles.

For example, for a particle that is one millimeter in thickness such as silicate coating would be about 5 microns thick. Preferably the coating will be on the outer 0.5% of the particle bead diameter, more preferably the outer 0.2% thereof.

Of course, when only partial coatings are applied and when greater percentages of silicate are utilized, as when only the bentonite agglomerates are coated, the silicate thicknesses will be greater, but preferably less than 2%. Normally, such thicknesses will be at least 0.05% of the particle thickness.

The products and processes of this invention possess many advantages, several of which have already been mentioned. With respect to the products, the application of silicate to particle surfaces, even when the entire particle is not covered with the silicate, improves the dispensing characteristics of such particle without having any adverse effects. Thus, detergent compositions of the types described herein, and the particulate components of such compositions mentioned, are easier to dispense from a charging compartment of an automatic washing machine of the European type than the control products untreated with silicate. This difference is most pronounced with respect to the agglomerated bentonite particles. The tests for comparing such results are practical use tests, employing a variety of different makes of such European washing machines, with the evaluator noting the number of particles remaining in the charging compartment after a normal charging and dispensing operations or after repeated such operations. To accentuate the differences and make the test more difficult, the walls of the charging compartment are first wet to promote adherence to them of the bentonite (and other materials). To simulate such a test one may sprinkle equal weights of test and control product onto a wet horizontal surface, allow them to stand for one or two minutes, and then direct a gentle spray of water onto the particles for a measured time, e.g. 30 seconds, after which the numbers of particles may be compared. By such tests the products of this invention show a marked improvement over the controls; normally one may expect to obtain less than half the number of particles still adhering to the pre-moistened surfaces when the "experimental" product is used, compared to the control. Often no particles

will be adhering to the pre-moistened surface when at least 0.15% of silicate is used, several particles will be sticking when at least 0.05% but less than 0.15% of silicate is employed, and an appreciable number of particles will be adhering when no silicate is present.

When most of the detergent will be charged to the washing tub in normal use of the automatic washing machine so that the retention of some particles in the charging chamber may not initially be more than psychologically objectionable, with repeated washings greater numbers may be retained, thereby changing the composition of the fabric softening detergent and possibly even significantly affecting the charge weight. Also, the appearance of the charging compartment with particles retained therein is unsatisfactory and can lead to consumer rejection of the product. Because of the different washing techniques employed in America, coating bentonite detergent particles with silicate may not be as important there but it is considered that the presence of the silicate on the particle will assist in making the detergent more stable and more freely flowing, especially in damp conditions, and will help to counteract any gelation of the bentonite under such conditions.

In addition to promoting dispensing, the silicate also has the desirable effect of preventing excessive foaming of the detergent composition in aqueous solution. The bentonite also helps to limit foaming and the combination is superior to the individual components. The silicate also appears to have a stabilizing effect on enzymes and bleaches coated with it and helps to prevent interaction between perfume components and other detergent constituents, thereby helping to stabilize the perfume. It can also have such an effect on colourants. Yet, these various advantages are obtained without the disadvantages of the product being excessively hydrophobic, because it is initially water soluble. It does not interfere with the desired quick dissolving and dispersing of the detergent components and does not appear to cause an objectionable buildup of hydrophobic deposits on washed and softened laundry. It does not interfere with the particular softening effect of the hydrophilic bentonite and does not interfere with the good detergency of the composition. The detergent compositions resulting are excellent laundry detergents and effectively soften washed laundry, as has been established by comparative tests against similar compositions containing neither bentonite nor silicate. The products are satisfactorily free flowing and of desired bulk density and appearance. They are also non-dusting which may at least in part be attributable to the silicate.

Processes in which silicate solutions or emulsions are sprayed onto detergent, bentonite and other detergent component particles are easily carried out and do not require special equipment. Due to the water solubility of the silicate it may be applied in an aqueous solvent

without adding other components to the detergent formula. Yet, it can also be emulsified or otherwise distributed with other detergent compounds. The processes lend themselves to 5 modification to allow different concentrations of siliconate on different detergent components. The coating materials do not gel or thicken objectionably, do not block spray nozzles and do not form gummy deposits in the spraying and mixing 10 equipment. The siliconate may be applied at room temperature because it does not require heating, as do some other protective coating materials. The siliconate can be retained principally on the surfaces of the particles, allowing less to be 15 employed while still producing the desired dispensing assisting effect. Also, apparently due to the nature of the siliconate or derivative thereof on the detergent or component particle, it is effective even when the particle is not completely 20 covered by it.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying 25 examples. Unless otherwise indicated, all parts are by weight and all temperatures in °C.

#### Example 1

A crutcher mix totalling 3,199.5 kilograms of material is made by reacting 364 kg of Dobane 30 JNQ (which contains 48.8% active ingredient which is dodecylbenzene sulphonic acid) and 167 kg of hydrogenated fatty acids (16 to 18 carbon atoms per mol of fatty acid) with 47 kg of caustic soda (38% Na<sub>2</sub>O) in an aqueous medium 35 containing a suitable proportion (to maintain the reaction) of 952 kg of city water (300 p.p.m. hardness, as CaCO<sub>3</sub>). The balance of such water is employed to cool the reaction mix, as desirable, and to dilute other components of the crutcher 40 mix. Subsequently there are added to the crutcher 242 kg of aqueous sodium silicate solution (Na<sub>2</sub>O:SiO<sub>2</sub>=1:2.4) at a 44.1% solids concentration, 7.5 kg of fluorescent stilbene type brightener, 7 kg of Sydex 808 (85% MgSiO<sub>3</sub> and 45 15% magnesium DTPA), 1,252 kg of hydrated sodium tripolyphosphate (TPP "H"), 54 kg of anhydrous sodium sulphate (99.5% pure) and 107 kg of a nonionic detergent, which may be considered as the condensation product of 11 50 mols of ethylene oxide with one mol of higher fatty alcohol having 12 to 15 carbon atoms per mol.

The crutcher mix is heated for about an hour, with stirring, so that its temperature rises to about 55 55°C, after which it is pumped to a spray drying tower where it is sprayed at elevated pressure through multiple spray nozzles into drying air at a temperature of about 300°C. Particles of a moisture content of about 12% result, most of 60 which are within the No's 10 to 100 sieve range (U.S. Sieve Series, which have openings 2000 microns (2 mms) and 149 microns across respectively). Particles outside this range are screened out.

65 63.1 Parts of the spray dried powder (bulk density of about 0.4 g/ml) are then blended with 0.3 part of prilled proteolytic enzyme (Alcalase, of 2 Anson units per gram, although Maxatase P 440,000 may be substituted), 20 parts of 70 granular sodium perborate and 16 parts of agglomerated bentonite. All such powders are of particle sizes within the particle size range for the spray dried detergent composition component but smaller particles of the enzyme and perborate. 75 may also be employed, down to about No. 200 (U.S. Sieve Series which has openings 74 microns across). The bentonite particles are composed of 82.3 parts of anhydrous bentonite, 16.1 parts of water, 1.5 parts of sodium silicate (previously 80 described) and 0.06 part of Acilan Brilliant Blue dye, with the dye being applied to the surface of the particles. The bentonite particles are made by agglomeration of more finely divided particles of bentonite (Laviosa AGB) with the dilute sodium 85 silicate solution (in the water, after which they are dyed. The bentonite employed is one which has been treated with sodium carbonate to replace calcium and magnesium therein with sodium and from which a natural content of gritty material has 90 been removed, after treatment, by centrifugal separation. Such processing methods for the bentonite will be described subsequently in this example. The moisture content of suitable agglomerated bentonite may be varied and can be 95 as low as 3%, when mixed with other components of the present softening detergent.

Onto the mixture of spray dried beads, enzyme, perborate and coloured bentonite particles, in an inclined drum mixer, there are sprayed 0.5 part of 100 the nonionic detergent, 0.25 part of Rhodorsil Siliconate 51 T (50% solution of potassium methyl silicate) and 0.25 part of detergent perfume. The spraying is regulated so that the sprayed liquid evenly coats the particles in the 105 mixer or tumbling drum to produce about 100 parts of uniform product.

The final product is of particle sizes within the range of No's 10 to 60 sieve (U.S. Sieve Series, which have openings 2000 microns and 250 110 microns across respectively), a bulk density of about 0.5 g/ml and a moisture content of about 12% (although on standing this may be reduced to about 8 to 10% e.g. 9%). The particulate fabric softening detergent resulting is non-dusting, free 115 flowing and attractive in appearance, with somewhat larger (averaging 20 to 200% greater in diameter) blue agglomerated bentonite particles contrasting with the other white particles. While the spray dried beads and the 120 bentonite agglomerates are distinct, the perborate and enzyme, especially when particles thereof are of sizes at the low end of the range mentioned, may appear to blend with the other beads, thus improving enzyme appearance. However, they are 125 not agglomerated and if not separate, are readily separable from the other such particles and from each other.

When the product described is subjected to practical laundry testing it is found to be an

excellent detergent with desirable fabric softening properties. When evaluated, it is noted that it is more readily dispensable, leaving fewer particles behind in the charging compartment of a

5 European type automatic washing machine, than a control in which the silicate coating is not present. This is especially important when the bentonite particles are larger, since they may tend more to adhere to wet chamber walls during

10 dispensing.

When the above experiment is repeated but with 100 kg of dodecylbenzene sulphonate acid, 1.324 kg of TPP "H" and 0.6 part of Rhodorsil Silicate 51 T being employed instead of the

15 amounts previously used the product resulting is of as satisfactory physical properties and functions but additionally is even more readily automatically dispensable, leaving no particles behind in the charging compartment of a

20 European type automatic washing machine.

In modifications of the above procedure the anionic detergent is replaced by equal weights, respectively, of sodium lauryl sulphate, sodium hydrogenated tallow alcohol sulphate and sodium

25 tallow alcohol polyethoxy (3EtO) sulphate.

Alternatively, mixtures of such materials, e.g. equal parts of sodium dodecylbenzene sulphonate and sodium hydrogenated tallow alcohol sulphate, are employed together. In all such cases

30 the final detergent composition resulting is one which is an excellent textile softening laundry detergent. All such products are also of improved dispensing characteristics, when tested by the methods previously described. Similar results are

35 also obtainable when, instead of the anionic detergent being varied, the nonionic detergent is changed, being replaced by a block copolymer of propylene oxide and ethylene oxide, such as Pluronic L-44 or L-62, nonyl phenol poly-

40 oxyethylene (12 EtO) glycol or a condensation product of C<sub>12-15</sub> fatty alcohol with 3 or 7 mols of ethylene oxide per mol, or with a mixture of two or more of such detergents, e.g. in equal parts. When half or all of the sodium tripolyphosphate is

45 replaced by NTA the final product is also a satisfactory detergent, with softening properties, and is of improved dispensing properties compared to a control of the same formula without the silicate.

50 When the soap is omitted from the formula diminished foam control results but otherwise the product is acceptable and is like those previously described. When the sodium perborate is replaced by other bleaching agents, such as sodium per-

55 sulphate, sodium perisophthalate or magnesium dimonoperoxyphthalate, good bleaching and cleaning by the product is still obtainable. When known activators for oxidizing agents are present bleaching may be effected by use of the

60 composition at lower temperatures than those near the boil (which are normally employed in the processes of this example to obtain maximum bleaching activity). When it is desired to include more silicate in the product the amount of silicate

65 is doubled by post-adding similarly sized hydrous

sodium silicate particles with the other post-added particulate solids. When sodium propyl silicate is substituted for potassium methyl silicate comparable products are obtainable and this is also the case when silicates of lesser degrees of water solubility are employed in replacement of some, e.g. 25%, of the other silicates.

The bentonite agglomerates employed in this

75 example are substantially regular spheres consisting essentially of bentonite with a small proportion of silicate binder and with a bluing colourant on the surface thereof. To make them, an Italian clay, low in exchangeable sodium, is

80 processed to increase the sodium content, swelling capacity and softening effects. First, such clay, containing a minor proportion, e.g. about 3%, of hard, black gritty mineral, is crushed and size reduced so that the particles thereof pass

85 through a No. 4 sieve (U.S. Sieve Series which has openings 4760 microns (4.76 mm) across), after which they are treated with an excess e.g. 50% excess, of sodium carbonate solution, such as one at a concentration of about 10%. The mix

90 is allowed to stand, with intervening periods of mixing, for a suitable time for reaction, such as about four hours, at which point sufficient ion exchange has occurred between the exchangeable calcium and magnesium of the clay

95 so that a typical analysis thereof is that given for Italian bentonite (after alkaline treatment) earlier in this specification. By such treatment the Na<sub>2</sub>O content of the clay has been increased significantly (about 2%) and the MgO and CaO

100 contents have been diminished by corresponding proportions. The clay is then dried, for example to a moisture content of about 5%, after which it is size reduced to particles that are desirably less than No. 100 sieve (U.S. Sieve Series which has

105 openings 149 microns across) (although sometimes larger sizes of particles may be present) and is subjected to centrifugal air separation in a cyclone separator (although size-separating techniques may also be employed) to

110 remove the grit. The grit-free bentonite, containing less than 0.1% of grit having a swelling capacity of about 5 ml/g and being of a viscosity of about 15 centipoises, at 6% concentration in water, and of a moisture content of about 7%, is

115 next agglomerated by the method described earlier herein, with the dilute sodium silicate solution being sprayed onto the surfaces of the moving particles while they are being tumbled in an inclined drum. Tumbling is continued until the

120 particles are of the desired size range and are satisfactorily rounded. At the end of the tumbling period, which may last for up to an hour, on the average, a dilute dye solution is sprayed onto the beads to colour them, and they are ready for

125 mixing with the other components to make a final detergent product.

#### Example 2

The procedures of Example 1 are varied by applying the silicate, in aqueous solution (20%

solids), as a finely divided spray (preferably with the spray droplets being "micron sized", e.g. 1 to 50 or 1 to 10 microns in diameter), or otherwise as satisfactorily small sized liquid droplets, to

5 each of the particulate components to be blended together separately before such blending. The various coated particles are all of bulk densities in the prescribed range (0.3 to 0.6 g/ml, e.g. 0.5 g/ml). Subsequently, the perfume is similarly

10 sprayed onto the mix. The nonionic detergent is not post-sprayed but instead, is incorporated in the crutcher mix. The resulting product is one which is also of improved dispensing properties. The siliconate coated agglomerated bentonite,

15 spray dried detergent composition beads (without bentonite), enzyme and perborate can all be separately produced and stored, and subsequently are useful for formulating fabric softening detergents of different compositions

20 and different desired properties, e.g. coated bentonite plus uncoated spray dried beads.

### Example 3

A softening detergent like that of the first formula of Example 1 is made from a crutcher mix of 10.24 parts of the dodecylbenzene sulphonic acid, 2.81 parts of the hydrogenated fatty acid, 0.81 part of the caustic soda, 26.54 parts of water, 37.2 parts of pentasodium tripolyphosphate (hydrated), 6.8 parts of sodium silicate solution, 0.21 part of fluorescent brightener, 1.46 parts of sodium sulphate and 3.0 parts of the nonionic detergent, added sequentially. This is spray dried by the method described in Example 1 to produce 62.5 parts of a product of similar bulk density and particle size. The spray dried particles are then mixed with 0.3 part of proteolytic enzyme, 20.0 parts of the sodium perborate granules, 16.0 parts of the agglomerated bentonite and 0.2 parts of Sydex 808, and onto

40 the tumbling powder mix there is sprayed a blend of 0.3 part of the detergent perfume and 0.4 part of  $C_{10-13}$  linear alkylate, and 0.15 part of potassium methyl siliconate is sprayed onto the product in suitable liquid state, preferably

45 dissolved in water (50% concentration). The product made is of better dispensing properties for dispensing from the charging compartment of an automatic washing machine in normal use. It exhibits a slightly greater foaming tendency than

50 the similar products of Example 1. When 0.3 part of the siliconate is used the dispensing properties of the detergent composition are further improved.

When, instead of employing an agglomerated sodium carbonate-treated Italian bentonite from which grit has been removed, as in Example 1, a competitive grit-free swelling clay product (Winkelmann agglomerate) or a Wyoming type bentonite, such as that sold under the trade name

55 Mineral Colloid No. 101 (formerly Thixogel No. 1) is employed, similar final products are obtained which are good softening detergents and are readily dispensed. Also, when other lower alkyl siliconates, such as sodium propyl siliconate, are

65 utilized, comparable results are obtainable. When the Acilan Blue dye, used to colour the bentonite agglomerates, is replaced by ultramarine blue, good colouring and bluing effects are also obtained. Similarly, when the siliconate is applied

70 only to the agglomerated bentonite, with the total proportion of siliconate in the product being the same, or 50% less in some cases, the properties of the detergent resulting are similar to those previously described and dispensing is also

75 improved, compared to a control.

### Example 4

When the proportions of the various components in the preceding Examples are modified  $\pm 10\%$ ,  $\pm 20\%$  and  $\pm 30\%$ , maintaining

80 them within the ranges previously given and keeping the ratios of anionic detergent to nonionic detergent within the range of about 1:1 to 3:1, the ratio of total detergent content to builder content within the range of about 1:3 to

85 1:8 and the ratio of sodium bentonite to total detergent within the range of about 1:1 to 2:1, products of properties similar to those described in Example 1 are obtained. Such is also the case when the water soluble builder salt(s) of Example

90 1 are replaced with zeolite A (20% hydrated) and when any of a variety of synthetic anionic and nonionic detergents is employed in admixture, optionally with an amphoteric detergent, such as one of the Miranol type. Also, the invention may

95 be used to improve the dispensing properties of various other bentonites and particulate detergent compositions of widely different formulas, densities (0.2 to 0.9 g/ml) and sizes (preferably No. 10—40 sieve; U.S. Sieve Series, 10 having

100 openings 2000 microns across and 40 openings 420 microns across).

### Claims

1. A particulate laundry composition or a component therefor which includes a dispensing assisting proportion of a siliconate or a dispensing assisting derivative thereof or both.

2. A laundry composition as claimed in Claim 1 which is a heavy duty laundering and textile softening particulate detergent composition,

110 useful for automatic machine washing of laundry in water and dispensable from a charging compartment of such a machine by action of water being fed through such compartment, which comprises a built synthetic organic

115 detergent which is an anionic or a nonionic detergent or a mixture thereof, a building proportion of builder for the synthetic organic detergent which is a water soluble or a water insoluble builder or a mixture thereof, and a

120 softening proportion of bentonite, with the bentonite being in particles with which there is included a dispensing assisting proportion of a siliconate and/or a dispensing assisting derivative thereof.

125 3. A laundry composition as claimed in Claim 1 or Claim 2 in which the dispensing assisting proportion is at least 0.15%.

4. A detergent composition as claimed in Claim 2 or Claim 3 which comprises 3 to 10% of a sodium salt of a synthetic anionic organic detergent which is a sulphonate or a sulphate or a mixture thereof, 1 to 5% of an nonionic detergent, 0 to 10% of a water soluble alkali metal soap, 20 to 75% of a builder for the synthetic organic detergent, 5 to 35% of a bleaching agent which releases oxygen in aqueous solution at elevated temperature, and 5 to 25% of bentonite.

5. A detergent composition as claimed in Claim 4 in which the sodium salt of the anionic detergent is a sodium linear higher alkylbenzene sulphonate in which the higher alkyl group is of 10 to 14 carbon atoms, a sodium higher fatty alcohol sulphate in which the higher fatty alcohol is of 10 to 16 carbon atoms, or a sodium higher fatty alcohol polyethoxy sulphate wherein the higher fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 20 ethoxy groups per mol, or a mixture thereof.

6. A detergent composition as claimed in Claim 4 or Claim 5 which comprises from 3 to 7% of sodium linear higher alkylbenzene sulphonate in which the higher alkyl group is of 11 to 13 carbon atoms.

7. A detergent composition as claimed in any one of Claims 4 to 6 in which the higher alkyl group of the sodium linear higher alkyl benzene sulphonate is a dodecyl group.

8. A detergent composition as claimed in any one of Claims 4 to 7 comprising about 5% of sodium linear dodecyl benzene sulphonate.

9. A detergent composition as claimed in any one of Claims 4 to 8 in which the nonionic detergent is a higher fatty alkoxy poly-lower alkoxy lower alkanol wherein the higher fatty alkoxy group is of 10 to 16 carbon atoms and the lower alkoxy and lower alkanol groups are of 2 to 3 carbon atoms and which contains from 3 to 20 lower alkoxy groups per mol.

10. A detergent composition as claimed in any one of Claims 4 to 9 in which the nonionic detergent comprises 2 to 5% of a higher fatty alkoxy poly-lower alkoxy lower alkanol wherein the higher fatty alkoxy group is of 12 to 15 carbon atoms, the lower alkoxy and lower alkanol groups are of 2 carbon atoms, and the molar ratio of higher fatty alkoxy to lower alkoxy is from 1:5 to 50 1:15.

11. A detergent composition as claimed in any one of Claims 4 to 10 in which the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 15 carbon atoms and 9 to 55 13 mols of ethylene oxide per mol of higher fatty alcohol.

12. A detergent composition as claim in any one of Claims 4 to 11 in which the nonionic detergent is about 3% of higher fatty alkoxy poly-lower alkoxy lower alkanol nonionic detergent wherein the higher fatty alkoxy group is of 12 to 15 carbon atoms, the lower alkoxy and lower alkanol groups are of 2 carbon atoms and the molar ratio of higher fatty alkoxy to lower alkoxy is about 1:11.

13. A detergent composition as claimed in any one of Claims 4 to 12 in which the soap is a soap of higher fatty acids of 10 to 24 carbon atoms per mol.

70 14. A detergent composition as claimed in any one of Claims 1 to 13 in which there is 2 to 6% of sodium soap of higher fatty acids of 14 to 18 carbon atoms per mol.

15. A detergent composition as claimed in any one of Claim 4 to 14 in which the soap is a sodium soap of hydrogenated tallow fatty acids.

16. A detergent composition as claimed in Claim 15 in which the soap is about 5% of sodium soap of hydrogenated tallow fatty acids.

80 17. A detergent composition as claimed in any one of Claims 4 to 16 in which the builder is a water soluble or a water insoluble builder or a mixture thereof.

18. A detergent composition as claimed in any one of Claims 4 to 17 in which the builder is 30 to 50% of water soluble builder salt.

19. A detergent composition as claimed in any one of Claims 4 to 18 in which the builder salt is primarily of pentasodium tripolyphosphate.

90 20. A detergent composition as claimed in Claim 19 in which the builder is about 35% of hydrated pentasodium tripolyphosphate.

21. A detergent composition as claimed in any one of Claims 4 to 20 in which the bleaching agent is sodium perborate.

22. A detergent composition as claimed in Claim 21 in which the bleaching agent is 15 to 25% of sodium perborate.

23. A detergent composition as claimed in Claim 22 in which the bleaching agent is about 20% of sodium perborate.

100 24. A detergent composition as claimed in any one of Claims 4 to 23 in which the bentonite particles are in the form of agglomerated particles produced after sodium carbonate treatment of bentonite containing magnesium and/or calcium to replace such magnesium and/or calcium with sodium, with resulting magnesium carbonate and/or calcium carbonate present with the 105 bentonite in the particles.

25. A detergent composition as claimed in any one of Claims 4 to 24 in which the bentonite is an agglomerate of smaller particles of ground sodium bentonite from which accompanying grit 110 has been removed after grinding and before agglomeration.

26. A detergent composition as claimed in any one of Claims 4 to 25 in which the bentonite swells in water, having a swelling capacity of at 115 least 1 ml/g.

27. A detergent composition as claimed in any one of Claims 4 to 26 in which the bentonite is of a swelling capacity in the range of 5 to 30 ml/g.

28. A detergent composition as claimed in any one of Claims 4 to 27 in which the bentonite has a viscosity, in 10% dispersion in water, of 5 to 30 centipoises.

29. A detergent composition as claimed in any one of Claims 4 to 28 in which the bentonite is of 130 a moisture content of at least 3%.

30. A detergent composition as claimed in any one of Claims 4 to 29 in which the bentonite is sodium bentonite.

31. A detergent composition as claimed in any 5 one of Claims 4 to 30 in which 10 to 20% of bentonite is present in the composition.

32. A detergent composition as claimed in Claim 31 in which 16% of bentonite is present in the composition.

33. A detergent composition as claimed in any 10 one of Claims 4 to 32 in which the particles are of sizes within the range of No. 10 to No. 100, U.S. Sieve Series (which have openings 2000 microns and 149 microns across respectively).

34. A detergent composition as claimed in any 15 one of Claims 4 to 33 in which the sodium higher alkyl benzene sulphonate, soap and builder salt are together in substantially homogeneous particles spray dried from the same crutcher mix,

35. A detergent composition as claimed in any 20 one of Claims 4 to 34 in which the agglomerated bentonite particles are of average particle sizes greater than the average particle sizes of the spray dried particles and the perborate particles.

36. A detergent composition as claimed in any 25 one of Claims 4 to 35 in which the bentonite particles are differently coloured from the detergent particles and from the perborate particles so that they are readily identifiable in the detergent composition.

37. A detergent composition as claimed in any 30 one of Claims 4 to 36 containing 1 to 5% of sodium sulphate, 0.1 to 2% of optical brightener dye and 0.1 to 1% of proteolytic enzyme.

38. A detergent composition as claimed in any 35 one of Claims 4 to 37 containing about 3% of sodium silicate, about 0.3% of proteolytic enzyme, about 0.6% of perfume, about 0.2% of optical brightener and about 9% of moisture.

39. A detergent composition as claimed in Claim 4 in which the sodium salt of the anionic detergent is a sodium linear higher alkylbenzene 40 sulphonate in which the higher alkyl group is of 10 to 14 carbon atoms, a sodium higher fatty alcohol sulphate in which the higher fatty alcohol is of 10 to 16 carbon atoms, or a sodium higher fatty alcohol polyethoxy sulphate wherein the higher fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 20 ethoxy groups per mol, or a mixture thereof, the nonionic detergent is a higher fatty alkoxy poly-lower alkoxy lower alkanol wherein the higher fatty 45 alkoxy group is of 10 to 16 carbon atoms and the lower alkoxy and lower alkanol groups are of 2 to 3 carbon atoms and which contains from 3 to 20 lower alkoxy groups per mol, the soap is a soap of higher fatty acids of 10 to 24 carbon atoms per 50 mol, the builder is a water soluble or a water insoluble builder or a mixture thereof, the bleaching agent is sodium perborate and the bentonite is of a moisture content of at least 3% and swells in water, having a swelling capacity of 55 at least 1 ml/g.

40. A detergent composition as claimed in Claim 39 which comprises from 3 to 7% of sodium linear higher alkylbenzene sulphonate in which the higher alkyl group is of 11 to 13 carbon atoms, 2 to 5% of a higher fatty alkoxy poly-lower alkoxy lower alkanol wherein the higher fatty alkoxy group is of 12 to 15 carbon atoms, the lower alkoxy and lower alkanol groups are of 2 carbon atoms, and the molar ratio of higher fatty 60 alkoxy to lower alkoxy is from 1:5 to 1:15, 2 to 6% of sodium soap of higher fatty acids of 14 to 18 carbon atoms per mol, 30 to 50% of water soluble builder salt, 15 to 25% of sodium perborate and 10 to 20% of sodium bentonite.

41. A detergent composition as claimed in Claim 40 in which the particles are of sizes within the range of No. 10 to No. 100, U.S. Sieve Series (which have openings 2000 microns and 149 microns across respectively), the sodium higher 65 alkyl benzene sulphonate, soap and builder salt are together in substantially homogeneous particles spray dried from the same crutcher mix, the sodium perborate is in separate or separable particles and the bentonite is in separate particles.

42. A detergent composition as claimed in Claim 41 in which the higher alkyl group of the sodium linear higher alkyl benzene sulphate is a dodecyl group, the nonionic detergent is a condensation product of a higher fatty alcohol of 70 12 to 15 carbon atoms and 9 to 13 mols of ethylene oxide per mol of higher fatty alcohol, the soap is a sodium soap of hydrogenated tallow fatty acids, the builder salt is primarily of penta-sodium tripolyphosphate and the bentonite particles are in the forms of agglomerates produced after sodium carbonate treatment of bentonite containing magnesium and/or calcium to produce sodium bentonite, with resulting magnesium carbonate and/or calcium carbonate 75 present with the bentonite in the particles.

43. A detergent composition as claimed in Claim 42 which comprises 1 to 5% of sodium sulphate, 0.1 to 2% of optical brightener dye and 0.1 to 1% of proteolytic enzyme, in which the 80 agglomerated bentonite particles are of average particle sizes greater than the average particle sizes of the spray dried particles and the perborate particles, and are differently coloured so that they are readily identifiable in the 85 detergent composition.

44. A detergent composition as claimed in Claim 43 in which the sodium bentonite is of a swelling capacity in the range of 5 to 30 ml/g and of a viscosity, in 10% dispersion in water, of 5 to 90 30 centipoises, and is an agglomerate of smaller particles of ground sodium bentonite from which accompanying grit has been removed after grinding and before agglomeration.

45. A detergent composition as claimed in Claim 44 comprising about 5% of sodium linear dodecyl benzene sulphonate, about 3% of higher fatty alkoxy poly-lower alkoxy lower alkanol anionic detergent wherein the higher fatty alkoxy group is of 12 to 15 carbon atoms, the lower 95 alkoxy and lower alkanol groups are of 2 carbon atoms, and the molar ratio of higher fatty alkoxy to lower alkoxy is from 1:5 to 1:15, 2 to 100 6% of sodium soap of higher fatty acids of 14 to 18 carbon atoms per mol, 30 to 50% of water soluble builder salt, 15 to 25% of sodium perborate and 10 to 20% of sodium bentonite.

atoms and the molar ratio of higher fatty alkoxy to lower alkoxy is about 1:11, about 5% of sodium soap of hydrogenated tallow fatty acids, about 20% of sodium perborate, about 16% of sodium bentonite, about 35% of hydrated pentasodium tripolyphosphate, about 3% of sodium silicate, about 0.3% of proteolytic enzyme, about 0.6% of perfume, about 0.2% of optical brightener and about 9% of moisture.

5 46. A detergent composition as claimed in Claim 4 in which the bentonite particles are in the form of agglomerated particles produced after sodium carbonate treatment of bentonite containing magnesium and/or calcium to replace such magnesium and/or calcium with sodium, with resulting magnesium carbonate and/or calcium carbonate present with the bentonite in the particles.

10 47. A detergent composition as claimed in Claim 46 in which the sodium bentonite agglomerate is of a swelling capacity in the range of 5 to 30 ml/g and of a viscosity, in 6% dispersion in water, of 5 to 30 centipoises, and is an agglomerate of smaller particles of ground sodium bentonite from which accompanying grit has been removed after grinding and before agglomeration.

15 48. A component for a laundry composition as claimed in Claim 1 which comprises agglomerated bentonite particles.

20 49. Agglomerated bentonite particles, useful for incorporation in a particulate heavy duty detergent composition for use in automatic washing machines which comprise such bentonite with which there is included a dispensing assisting proportion of a silicate and/or dispensing assisting derivative thereof.

25 50. Agglomerated bentonite particles as claimed in Claim 48 or Claim 49 in which the dispensing assisting proportion is at least 0.15%.

30 51. Agglomerated bentonite particles as claimed in Claim 49 or Claim 50 which are of sizes in the range of No's 10 to 100, U.S. Sieve Series, (which have openings 2000 microns across and 149 microns across respectively).

35 52. Agglomerated bentonite particles as claimed in Claims 49, 50 or 51 which are formed after sodium carbonate treatment of bentonite containing magnesium and/or calcium to produce sodium bentonite, with the resulting magnesium carbonate and/or calcium carbonate present with the bentonite in the particles.

40 53. A laundry composition as claimed in Claim 1 which is a particulate synthetic organic detergent composition which comprises a built synthetic organic detergent which is an anionic or a nonionic detergent or a mixture thereof, a building proportion of a builder for the synthetic organic detergent which is a water soluble or a water insoluble builder or a mixture thereof.

45 54. A laundry composition as claimed in Claim 53 which is in spray dried bead form of particle sizes within the range of No's 10 to 100 (U.S. Sieve Series which have openings 2000 microns across and 149 microns across respectively),

50 which comprises about 3 to 7 parts of sodium linear higher alkylbenzene sulphonate in which the higher alkyl group is of 11 to 13 carbon atoms, 2 to 4 parts of higher fatty alkoxy poly-lower alkoxy lower alkanol wherein the higher fatty alkoxy group is of 12 to 15 carbon atoms and the molar ratio of higher fatty alkoxy to lower alkoxy is from 1:5 to 1:15, 2 to 6 parts of sodium soap of higher fatty acids of 14 to 18 carbon atoms per mol, 30 to 50 parts of pentasodium tripolyphosphate and 0 to 15 parts of adjuvants, with the total being 100%.

55 55. A component for a laundry composition as claimed in Claim 1 which is particles of sodium perborate of sizes in the range of No's 10 to 200, (U.S. Sieve Series which have openings 2000 microns across and 74 microns across respectively).

60 56. A component for a laundry composition as claimed in Claim 1 which is particles of enzyme of sizes in the range of No's 10 to 200 (U.S. Sieve Series which have openings 2000 microns across and 74 microns across respectively).

65 57. A particular laundry composition or a component therefor as claimed in any one of the preceding claims in which the silicate is an alkali metal lower alkyl silicate.

70 58. A composition or a component as claimed in Claim 57 in which the alkali metal lower alkyl silicate is water soluble, the alkali metal thereof is potassium or sodium, and the lower alkyl group thereof is of 1 to 3 carbons.

75 59. A composition or component as claimed in Claim 57 or 58 in which the silicate is potassium methyl silicate.

80 60. A composition or component as claimed in Claim 57, 58 or 59 containing 0.05 to 3% of the silicate or derivative thereof.

85 61. A composition or component as claimed in Claim 60 containing 0.05 to 1% of the silicate or derivative thereof.

90 62. A composition or component as claimed in Claim 61 containing 0.15 to 0.3% of the silicate or derivative thereof.

95 63. A composition or component as claimed in Claim 62 containing about 0.1% of the silicate or derivative thereof.

100 64. A detergent composition as claimed in Claim 1 which comprises 3 to 10% of a sodium salt of a synthetic anionic organic detergent which is a sulphonate or a sulphate or a mixture thereof, 1 to 5% of a nonionic detergent, 0 to 10% of a water soluble alkali metal soap, 20 to 75% of a builder for the synthetic organic detergent, 5 to 35% of a bleaching agent which releases oxygen in aqueous solution at elevated temperature, and 5 to 25% of bentonite, and an alkali metal lower alkyl-silicate, and/or dispensing assisting derivative thereof.

105 65. A detergent composition as claimed in Claim 64 in which the sodium salt of the anionic detergent is a sodium linear higher alkylbenzene sulphonate in which the higher alkyl group is of 10 to 14 carbon atoms, a sodium higher fatty alcohol sulphate in which the higher fatty alcohol

is of 10 to 16 carbon atoms, or a sodium higher fatty alcohol polyethoxy sulphate wherein the higher fatty alcohol is of 10 to 18 carbon atoms and which contains from 3 to 30 ethoxy groups per mol, or a mixture thereof, the nonionic detergent is a higher fatty alkoxy poly-lower alkoxy lower alkanol wherein the higher fatty alkoxy group is of 10 to 16 carbon atoms and the lower alkoxy and lower alkanol groups are of 2 to 5 carbon atoms and which contains from 3 to 20 lower alkoxy groups per mol, the soap is a sodium soap of higher fatty acids of 10 to 24 carbon atoms per mol, the builder is a water soluble salt or a water insoluble zeolite or a mixture thereof, the bleaching agent is sodium perborate, the bentonite is of a moisture content of at least 3% and swells in water, with the swelling capacity thereof being at least 1 ml/g and the alkali metal lower alkyl silicate is water soluble, the alkali metal thereof is potassium or sodium, and the lower alkyl group thereof is of 1 to 3 carbons.

66. A detergent composition as claimed in Claim 65 which comprises from 3 to 7% of sodium linear higher alkylbenzene sulphonate in which the higher alkyl is of 11 to 13 carbon atoms, 2 to 4% of a higher fatty alkoxy poly-lower alkoxy lower alkanol wherein the higher fatty alkoxy is of 12 to 15 carbon atoms, the lower alkoxy and lower alkanol groups are of 2 carbon atoms and the molar ratio of higher fatty alkoxy to lower alkoxy is from 1:5 to 1:15, 2 to 6% of sodium soap of higher fatty acids of 14 to 18 carbon atoms per mol, 30 to 50% of water soluble builder salt, 15 to 25% of sodium perborate, 10 to 20% of sodium bentonite and 0.15 to 0.3% of potassium methyl silicate.

67. A detergent composition as claimed in Claim 66 in which the higher alkyl group of the sodium linear higher alkyl benzene sulphonate is dodecyl, the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 15 carbon atoms and 9 to 13 mols of ethylene oxide per mol of higher fatty alcohol, the soap is a sodium soap of hydrogenated tallow fatty acids, the builder salt is primarily of pentasodium tripolyphosphate, the bentonite particles are in the form of agglomerates produced after sodium carbonate treatment of bentonite containing magnesium and/or calcium to produce sodium bentonite, with resulting magnesium carbonate and/or calcium carbonate present with the bentonite in the particles, and the particles thereof are coated or partially coated with potassium methyl silicate.

68. A detergent composition as claimed in Claim 67 comprising about 5% of sodium linear dodecyl benzene sulphonate, about 3% of higher fatty alkoxy poly-lower alkoxy lower alkanol nonionic detergent wherein the higher fatty alkoxy is of 12 to 15 carbon atoms, the lower alkoxy and lower alkanol are of 2 carbon atoms and the molar ratio of higher fatty alkoxy to lower alkoxy is about 1:11, about 5% of sodium soap of hydrogenated tallow fatty acids, about 20% of sodium perborate, about 16% of sodium

bentonite, about 35% of hydrated pentasodium tripolyphosphate, about 3% of sodium silicate, about 0.1% of potassium methyl silicate, about 0.3% of proteolytic enzyme, about 0.3% of perfume, about 0.2% of optical brightener and about 12% of moisture.

69. Agglomerated bentonite particles as claimed in Claim 1 which contain from 0.05 to 3% of alkali metal lower alkyl silicate and/or dispensing assisting derivative thereof at the surfaces of the particles.

70. Agglomerated bentonite as claimed in Claim 69 which are coated or partially coated by 0.05 to 1% of potassium methyl silicate.

71. A detergent composition as claimed in Claim 1 which is in spray dried bead form of particle sizes within the range of No's 10 to 100 (U.S. Sieve Series which have openings 2000 microns across and 149 microns across respectively), which comprises about 3 to 7 parts of sodium linear higher alkylbenzene sulphonate in which the higher alkyl group is of 11 to 13 carbon atoms, 2 to 4 parts of higher fatty alkoxy poly-lower alkoxy lower alkanol wherein the higher fatty alkoxy group is of 12 to 15 carbon atoms and the molar ratio of higher fatty alkoxy to lower alkoxy is from 1:5 to 1:15, 2 to 6 parts of sodium soap of higher fatty acids of 14 to 18 carbon atoms per mol, 30 to 50 parts of pentasodium tripolyphosphate and 0 to 15 parts of adjuvants, with the total being 100%, and the particles of which are at least partially coated by 0.05 to 1% of potassium methyl silicate.

72. Sodium perborate particles as claimed in Claim 1 which are coated with from 0.05 to 1% of potassium methyl silicate.

73. Enzyme particles as claimed in Claim 1 which are coated with from 0.05 to 1% of potassium methyl silicate.

74. A laundry composition as claimed in Claim 1 substantially as specifically described herein with reference to the accompanying examples.

75. A method of manufacturing a heavy duty laundry and textile softening particulate detergent composition, useful for automatic machine washing of laundry in water and dispensable from a charging compartment of such a machine by action of water being fed through such compartment, which includes a built synthetic organic detergent which is an anionic or a nonionic detergent or a mixture thereof, a building proportion of a builder for the synthetic organic detergent which is a water soluble or a water insoluble builder or a mixture thereof, and a softening proportion of bentonite, with the bentonite being in particles with which there is included a dispensing assisting proportion of a silicate or a dispensing assisting derivative thereof or both, which comprises agglomerating particles of bentonite from finely divided from, passing through a No. 100 sieve (U.S. Sieve Series which has openings 149 microns across) and with over 50% thereof passing through a No. 200 sieve (U.S. Sieve Series which has openings 74 microns across), into agglomerates of particle

sizes within the range of No's 10 to 100 sieves (U.S. Sieve Series, No. 10 has openings 2000 microns across), spray drying an aqueous crutcher mix of the synthetic organic detergent and the 5 builder to detergent composition particles of sizes within the No's. 10 to 100 sieve range (U.S. Sieve Series), blending the bentonite agglomerate particles and spray dried detergent composition particles and applying to the surfaces of such 10 particles a dispensing assisting proportion of a silicate or a dispensing assisting derivative thereof or both.

76. A method as claimed in Claim 75 in which 0.05 to 1% of potassium methyl silicate is 15 sprayed onto the surfaces of the particles to at least partially coat them.

77. A method of manufacturing a heavy duty laundering detergent composition, useful for automatic machine washing of laundry in water 20 and dispensable from a charging compartment of such a machine by action of water being fed through such compartment, which includes a built synthetic organic detergent which is an anionic or a nonionic detergent or a mixture thereof, and a 25 building proportion of a builder for the synthetic organic detergent which is a water soluble or a water insoluble builder or a mixture thereof which comprises drying an aqueous crutcher mix of the synthetic organic detergent and the builder to 30 particles of sizes within the No. 10 to 100 sieve range (U.S. Sieve Series), and applying to the surface of such particles a dispensing assisting

proportion of a silicate or a dispensing assisting derivative thereof or both.

78. A method as claimed in Claim 77 in which the detergent includes sodium dodecyl benzene sulphonate, the builder is pentasodium tripolyphosphate or NTA or a mixture thereof, and 0.05 to 1% of potassium methyl silicate is sprayed 40 onto the surfaces of the spray dried particles to at least partially coat them.

79. A method of manufacturing agglomerated bentonite particles, useful for incorporation in a particulate heavy duty detergent composition

45 which is dispensable from the charging compartment of an automatic washing machine by action of water being fed through such compartment, which comprises applying to surfaces of agglomerated bentonite particles a 50 dispensing assisting proportion of a silicate or a dispensing assisting derivative thereof or both.

80. A method as claimed in Claim 79 in which the agglomerated bentonite particles are of particle sizes within the range of No's 10 to 100 55 sieve (U.S. Sieve Series), and are agglomerates of essentially grit-free particles of sodium bentonite which pass through a No. 100 sieve (U.S. Sieve Series) and of which over 50% pass through a No. 200 sieve (U.S. Sieve Series), and 60 wherein 0.05 to 1% of potassium methyl silicate is sprayed onto surfaces of the agglomerated particles to at least partially coat them.

